



# Predicting pH dependencies of electrode surface reactions in electrocatalysis



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## ABSTRACT

It is shown how to adopt the Nernst equation to electrode potential-dependent Gibbs energies, calculated for reactants and products from density functional theory, to make predictions of reversible potentials for redox reactions on electrode surfaces in electrolytes of any pH. The theory is general because any spectator species may be included in electrochemical interface. We demonstrate its application to H and OH deposition on Pt(111).

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## 1. Introduction

Little is known from experiment about the dependence of the compositions, structures, and properties of species adsorbed on an electrode surface on the potential or the pH of the bulk electrolyte. Theory is beginning to provide insight [1–3]. Recently we reported that the observed [4,5], ~50 mV shifts in onset potentials for under potential deposited (UPD) H(ads) and OH(ads) on Pt(111) between strongly acidic and strongly alkaline electrolytes could be calculated with quantum theory [3]. To be able to do this depended on having the ability to calculate the Gibbs energies of the reactants and products as functions of electrode potential. This was accomplished using a two-dimensional density functional theory (DFT) that includes surface charging to set a potential and a modified Poisson-Boltzmann treatment of the electrolyte polarization response to the charging [6,7]. The calculated Gibbs energy equilibrium conditions, which specified the reversible potentials for the reactions, included  $H^+(aq)$ , modeled as  $H_3O^+(H_2O)_3(aq)$ , or  $OH^-(aq)$ , modeled as  $OH^-(H_2O)_3(aq)$ , and  $H_2O(aq)$ , modeled as  $(H_2O)_4(aq)$ , as reactants or products, so that the information about the strongly acid and strongly alkaline bulk electrolytes was included in determining the predicted reversible potentials. Here with use of the Nernst equation a formula is derived for calculating the reversible potentials at any pH and tested over 14 values of pH for the onsets of UPD H(ads) and OH(ads) formation.

In the predictions of onset potentials for H(ads) and OH(ads) on Pt(111) in [3], the compositions of the adsorbed molecular layers were unchanged at low and high values of pH. In determining the onset potential for UPD H(ads) formation, the initial and final states included no  $H_2O$  molecules because they interact weakly with Pt(111) and H

(ads). In determining an onset potential for OH(ads) formation, since water is a reactant, the initial state was assigned 2/3 ML coverage in a hexagonal overlayer commensurate with the Pt(111) surface structure. The final state had 1/6 ML OH(ads) and 1/2 ML  $H_2O(ads)$ , one third of which were hydrogen bonded to the adsorbed OH.

The assigned pH was modeled computationally as follows:

For pH = 0 acidic electrolyte, the H(ads) forming reaction was



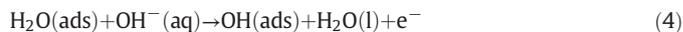
and for pH = 14 alkaline electrolyte, the reaction forming H(ads) was



For pH = 0 electrolyte, the OH(ads) forming reaction was



and for pH = 14 electrolyte the OH(ads) forming reaction was



In the above equations the assignments of pH were made by setting the compositions of the bulk electrolytes. We showed in [3] that for reduction reactions the potential-dependent product energy curve in pH = 0 acidic solution is more stable than the curve for pH = 14 alkaline solution by the autoionization energy of water, calculated to be 0.845 eV (0.828 eV is the experimental value). Crossing points with the reactant energy curves yielded the reversible potentials for acid and alkaline electrolytes. We propose now that reversible potentials for intermediate values of pH can be calculated by shifting the reduction product Gibbs energy curve in accordance with the desired pH to determine the crossing point. For example, to find the reversible potential for

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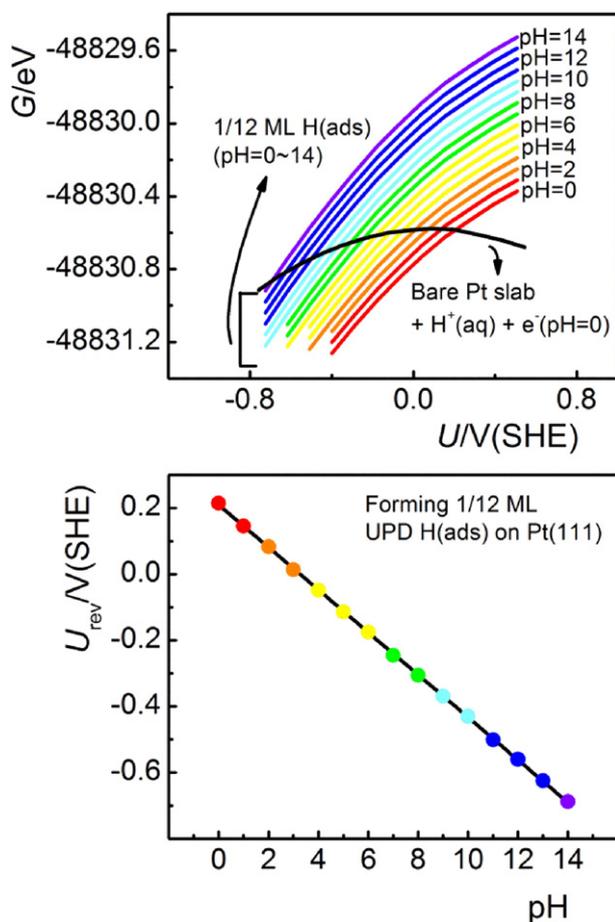
pH = 6 electrolyte, one destabilizes the product Gibbs energy curve for the pH = 0 electrolyte by  $(6 / 14) \times 0.845$  eV.

## 2. Theory

To understand why the above proposed method for predicting reversible potentials in solutions of intermediate values of pH is physically based, the details of the calculation method need to be explained. In our approach, the electrode potential is varied by changing the amount of charge added to the translational cell when performing two-dimensional density functional theory (DFT) band calculations based on atomic orbitals and pseudopotentials. When this is done, the potential,  $U$ , relative to the standard hydrogen electrode (SHE) of the electrode being modeled is a function of the thermodynamic workfunction of the SHE, for which 4.454 eV is calculated, and the calculated Fermi energy,  $E_f$ , of the two-dimensional slab electrode:

$$U(q) = -4.454 \text{ V} - E_f(q)F \quad (5)$$

Here  $q$  is the value of charge added to the translational cell and  $F$  is the Faraday constant. In response to the electrode charging, the electrolyte is polarized at the interface and this is modeled using a modified Poisson-Boltzmann theory, along with dielectric continuum, all calculated to self-consistency. The theory is parameterized for ionic strength = 1 with 3.0 Å diameter cations and anions, implicitly including hydration, and 298.15 K temperature. Complete details are in [7].



**Fig. 1.** Series of Eq. (12) plots for different values of pH:  $G(U)$  for  $1/12$  ML H(ads) on Pt (111) over a range of pH values and  $G(U)$  plot for bare Pt slab +  $H^+(aq) + e^-(pH = 0)$  (top panel) and the resulting  $U_{rev}$  versus pH curve (bottom panel). When extrapolation to zero coverage and the Langmuir statistical contributions are added, the  $U_{rev}$  values, as explained in Ref. [3], all increase by about 0.15 eV.

The modified Poisson-Boltzmann theory calculates the interaction between the explicit reactant or product surface species and the electrolyte within the double layer and the early diffuse region as the surface charge and potential are varied. There is no interaction between ions in the bulk solution with the adsorbed reactants or products. Consequently, the potential-dependent Gibbs energy curve for the reduced adsorbed product in, for example, acidic electrolyte can be used for solutions with other values of pH besides pH = 0 and pH = 14 to make first principles predictions of reversible potentials. To do this we will use the equation for the calculated auto ionization energy of water:

$$\Delta_w G^0 = RT/2.3026 (\text{pH} + \text{pOH}) = 0.845 \text{ eV} \quad (6)$$

and the Nernst equation at 298.15 K for a reduction reaction involving one proton and one electron,

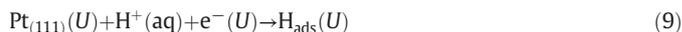
$$U(\text{pH} \neq 0) = U(\text{pH} = 0) - (0.05916 \text{ V})\text{pH} \quad (7)$$

Since the log of the calculated water autoionization constant,  $\text{p}K_w$ , is 14.283 instead of 14.00, we scale Eq. (7) by adding 0.0012 V to 0.05916 V so that the potential shift between pH = 0 and pH = 14 occurs in equal increments and equals the calculated  $-0.845$  V at pH = 14. Having done this we write

$$U(\text{pH} \neq 0) = U(\text{pH} = 0) - (0.0604 \text{ V})\text{pH} \quad (8)$$

In this equation, the addition of 0.0012 V to 0.05915 V accounts for the 0.017 eV calculated overestimation of the  $H_2O$  autoionization energy.

To find the reaction Gibbs energy,  $\Delta_{\text{react}}G$ , for the reaction



we use Eq. (8) in the formula for the energy of the electron

$$G(e^-) = -4.454 \text{ eV} - FU \quad (10)$$

to find  $\Delta_{\text{react}}G$ :

$$\Delta_{\text{react}}G(U) = G[\text{H}_{\text{ads}}(U)] - G[\text{Pt}_{(111)}(U)] - G[\text{H}^+(\text{aq})] + 4.454 \text{ eV} + FU - 0.0604 \text{ pH(eV)} \quad (11)$$

This is rewritten as

$$G[\text{H}_{\text{ads}}(U)] = \Delta_{\text{react}}G(U) + G[\text{Pt}_{(111)}(U)] + G[\text{H}^+(\text{aq})] - 4.454 \text{ eV} - FU + 0.0604 \text{ pH(eV)} \quad (12)$$

In general

$$G[\text{Red}(U)] = \Delta_{\text{react}}G(U) + G[\text{Ox}(U)] + G[\text{H}^+(\text{aq})] - 4.454 \text{ eV} - FU + 0.0604 \text{ pH(eV)} \quad (13)$$

We see from these equations that at any pH the energy of the reduction product is the energy of reaction plus the energy of the oxidized reactant. For a given pH, a potential  $U$  for which  $\Delta_{\text{react}}G(U) = 0$  is the reversible potential,  $U_{rev}$ .

## 3. Results and discussion

One way to locate the reversible potentials from the calculated potential-dependent Gibbs energies is from the graphical intersections of the oxidized reactant and reduced product energies for the pH values of interest, as done in Figs. 1 and 2. Fig. 1 is for a model for the onset potential for UPD H(ads) formation on Pt(111) and shows the series of reduced product curves for UPD hydrogen deposition for pH values of 0, 1, ..., 14 and their intersections with the oxidized reactant curve at pH = 0. From the intersections the  $U_{rev}$  versus pH curve shown in the lower

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